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# ETHYLENE AND AROMATICS BY CARBONIZATION OF CANNEL COAL

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The low-temperature carbonization of coal is a possible alternative to the cracking of crude oil for the production of ethylene and aromatics. The previous investigations reported by this laboratory were concerned with the carbonization of lignites.[1] It was found that if lignites were carbonized at a low temperature in order to obtain the maximum yield of tar and this tar cracked without being allowed to condense, acceptable yields of ethylene, propylene and aromatics could be obtained. Once the low temperature tar is allowed to condense, however, large amounts of char and heavy residue are formed in the cracker and the yields of the desired products are small. It was concluded from this work that this process could be commercially important if the cost of crude oil increases enough to offset the high initial capital cost.

The present investigation was concerned with the use of West Virginia and Kentucky cannel coals in this process. Cannel coal is a high volatile, non-coking coal and occurs in lenticular pockets in bituminous coal beds. It was hoped that the higher yields which would certainly be obtained with these coals, and therefore the lower capital investment required for the same production, would more than offset the increased cost of the coal.

## EXPERIMENTAL

### Equipment

The equipment used in this work is very similar to that used in the earlier work. The evolved volatile matter passed from a batch carbonizer through the cracker into the collection train, which consisted of a water-jacketed receiver, condenser, and two low-temperature absorbers. These absorbers consisted of jacketed pyrex columns packed with steel wool. The noncondensable gas passed through a cotton trap and then through a wet-test gas meter, which measured the volume of the evolved gas. After leaving the wet-test gas meter, the gas passed into a solenoid-actuated valve which allowed a fraction of the gas to be collected in a gas holder. The remainder was vented to the atmosphere.

The carbonizer used in these experiments was similar to that used in the lignite experiments, except that it was modified so that superheated steam could be blown through the coal during carbonization. It was made from a two inch stainless steel pipe, 24 inches in length. Near the top of the retort, a one-half inch pipe was provided as a take-off for the volatile matter. A one inch plug fitted with a thermocouple well was used at the top of the carbonizer for the introduction of the coal. A removable steel sparger was provided at the bottom of the carbonizer for the introduction of the superheated steam and the removal of the char. Heat for the carbonizer was provided by electric furnaces controlled by means of Variacs.

The cracking reactors were 36 inches long and were fabricated of Vycor tubing of 31 mm outside diameter. A concentric 9 mm Vycor tube, through the entire length of the cracking tube, allowed a thermocouple to be placed inside the tube and the cracking temperature to be measured for any point in the tube. The cracking temperature was controlled by the temperature near the exit of the reactor. The cracker was heated with resistance tape wound directly on the tubing and the electric current controlled by a Variac. Different average retention times were obtained by using two, three or four of these reactors in series.

## Coals Used

Samples of four different cannel coals were used in this work. Three were from West Virginia - Gay Mine, Logan County; Stollings Mine, Madison County; and Dorothy Mine, Boone County; one was from the Big Chief Mine, Letcher County, Kentucky. The samples which were received as 6 to 8 inch lumps were crushed, and the fraction which passed through a 3-1/2 mesh and remained on a 10 mesh screen was used in the experiments.

Table 1

| Proximate Analysis | Gay | Stollings | Dorothy | Big Chief |
|---|---|---|---|---|
| Moisture | 0.31% | 0.56% | 0.63% | 0.46% |
| Net Volatile | 48.46 | 54.86 | 61.05 | 53.07 |
| Fixed Carbon | 37.42 | 34.26 | 32.52 | 41.49 |
| Ash | 13.81 | 10.32 | 5.80 | 4.98 |
| **Ultimate Analysis** | | | | |
| Hydrogen | 6.56 | 7.04 | 7.71 | 7.29 |
| Carbon | 74.52 | 74.79 | 78.84 | 80.96 |
| Nitrogen | 0.67 | 1.22 | 0.88 | 1.23 |
| Sulfur | 0.52 | 1.24 | 0.86 | 0.77 |
| Oxygen | 3.92 | 5.39 | 5.91 | 4.77 |
| **Fisher Assay** | | | | |
| Oil, gal/ton | 85.8 | 90.6 | 104.2 | 86.5 |
| Water, gal/ton | 2.4 | 3.6 | 3.8 | 3.4 |
| Gas and loss, % | 9.1 | 9.2 | 10.9 | 6.7 |
| Sp. Gr. oil 60/60°F | 0.9056 | 0.9106 | 0.9079 | 0.9022 |

## PROCEDURE

Cannel Coal (500 grams) was charged into the carbonizer and the cracker temperature brought up to the predetermined level. Then the temperature of the carbonizer was slowly and uniformly raised from room temperature to a maximum of 550°C. When the carbonizer reached 300°, superheated steam at 500° was introduced into it. After the experiment, the carbonizer was allowed to cool to room temperature and the train disassembled, and the contents of the receiver and two absorbers steam distilled. The steam-distilled oil was then fractionated, and the fractions examined by mass spectrometry. The residual oil and tar in the distillation pot plus any increase in weight of the absorbers was designated as heavy oil. The volume of gas produced was measured with the wet-test gas meter and samples of the gas examined by mass spectrometry.

Exploratory experiments indicated that the primary process variables were cracking temperature, retention time and the steam-coal ratio. Therefore the effect of these three process variables at three different levels were investigated on the cannel coal from the Gay Mine, using nine experiments in a "Latin Square" arrangement. With this arrangement, the effect of a single variable can be determined with the effects, first order at least, of the other variables confounded or cancelled out. The levels of the process variables that were chosen were:

Cracking temperature - 800°, 850°, and 900°.

Average retention time - 0.5, 0.7, and 0.9 seconds.

Steam-to-coal ratio - 1.0, 1.25, and 1.5.

The "average retention time" deserves some comment. Since a batch carbonizer was used in these experiments, the rate of volatile generation in the carbonizer varied within rather wide limits as the carbonizer temperature was raised from 300° to 550°. Because of this, the gas velocity through the crackers, and therefore the retention time in the cracker also, varied within rather wide limits. "The average retention time" was calculated on the basis of the total volume of volatiles generated and volume of the crackers used in the experiment. These "average retention times" can only be used as guides; all that can be said for certain is that the retention times are in the ratios two, three and four.

Another problem which arises with regard to the interpretation of the effects of retention time is that the actual retention time is affected by the steam-coal ratio used. When more steam is passed through the carbonizer, the space velocity is increased, and therefore the retention time in the cracker correspondingly decreased. Because of this, the effects of average retention time and steam-coal ratio are interrelated despite the Latin Square arrangement of the data. This must be taken into account when interpreting the retention time data.

## RESULTS

Analysis of the products obtained in these experiments makes it possible to evaluate the effects of the process variables on the yields of the various products. Since all of the volatile matter passed through the cracker, the volume and composition of the evolved gases and oils was affected by all the process variables, that is, cracking temperature, retention time, and steam-coal ratio. The character of the char produced, however, could only be affected by the steam-coal ratio.

### Effect of Process Variables on Gas Produced

The composition of the gas evolved from the coal varies as different levels of the process variables are employed. Some constituents of the gas are affected greatly by the process variables, others, very little.

The chief components of the gas are ethylene, ethane, acetylene, propylene, butadiene, methane, hydrogen, and carbon monoxide and dioxide. These comprise at least 98% of the total gas produced.

The process variables have little or no effect on the total yield of gas, at least at the levels investigated. It might be expected that the higher cracking temperatures and longer retention times would produce more gas, but this is not the case.

The yield of ethylene, too, is not particularly affected by the process variables. However, the best yield was produced at a cracking temperature of 850°, an average retention time of 0.5 seconds, and a steam-coal ratio of 1.25.

The lowest cracking temperature and the shortest retention time investigated result in the production of the largest amount of ethane. Apparently more of the ethane is converted to ethylene at the more rigorous cracking conditions. At a cracking temperature of 800°, 24.8 pounds/ton is obtained, while at 900°, only 9.9 pounds/ton is obtained. The steam-coal ratio, however, does not seem to have any significant effect.

As might be expected, the highest yield of acetylene is obtained at the highest cracking temperature. At a cracking temperature of 800°, only 8.1 pounds/ton is obtained, but this is raised to 22.3 pounds/ton by increasing the cracking temperature to 900°. The steam-coal ratio is not nearly so important, but the production of acetylene is favored by the higher ratio. Perhaps surprisingly, the retention time has only little effect.

There is a substantial decrease in the yield of propylene when the higher cracking temperatures and longer retention times are employed. At a cracking temperature of 800°, 64.6 pounds/ton is obtained, but this falls to only 23.8 pounds/ton at 900°. Similarly, increasing the average retention time from 0.5 to 0.9 seconds resulted in a decrease in the yield of propylene from 59.8 to 32.1 pounds/ton. The steam-coal ratio, however, had comparatively little effect.

The yield of butadiene decreases rapidly as the cracking temperature and retention time are increased. At a cracking temperature of 800°, 22.0 pounds/ton is obtained, but at 900° only 11.2 pounds/ton is obtained. Similarly, increasing the retention time from 0.5 to 0.9 seconds decreases the yield of butadiene from 20.9 to 12.7 pounds/ton. The best steam-coal ratio for the production of butadiene is 1.25.

The process variables do not greatly affect the yield of methane. On the average, the methane yield is about 150 pounds/ton.

As might be expected, greater quantities of hydrogen are produced at the more rigorous cracking conditions. At a cracking temperature of 800°, a ton yields 12 pounds of hydrogen, at 900°, 19.4 pounds. Increasing the retention time from 0.5 to 0.9 seconds, similarly raises the yield of hydrogen from 13.5 to 17.1 pounds/ton. An increase in the steam-coal ratio from 1.0 to 1.5 decreases the amount of hydrogen obtained from a yield of 17 pounds/ton to 14 pounds/ton, probably because of its effect on the retention time.

The yield of carbon dioxide is quite constant at 15 pounds/ton at all levels of the process variables studied, and only cracking temperature has much effect on the yield of carbon monoxide. When the cracking temperature is raised from 800° to 900°, the yield of carbon monoxide increases from 40.9 to 72.2 pounds/ton.

Effect of Process Variables on Light Oil Produced

The process variables at the levels studied have no significant effect on the total yield of light oil. It might be expected that higher temperatures and longer retention times would favor the production of light oil owing to the conversion of heavy oil to light oil at the more rigorous conditions, but this is not true. Evidently, if more light oil is produced, more light oil is also converted into gaseous hydrocarbons. At all the conditions studied, the yield of light oil was about 115 pounds/ton.

The light oil contains a large number of compounds. The more easily identifiable components of the mixture are benzene, toluene, styrene, $C_2$ benzenes, indene, indan, and/or methylstyrene, naphthalene, and methyl naphthalene. These components comprise 58 to 73% of the total. The remainder is made up of more highly substituted benzenes, styrenes, and naphthalenes. Only the effects of the process variables on the production of benzene, toluene, styrene, and naphthalene will be discussed, since these are the most commercially important components.

The yield of benzene as a function of retention time shows a definite maximum at 0.7 seconds; and as a function of steam-coal ratio, a definite minimum at a ratio of 1.25. However, the levels of cracking temperature employed seem to have no significant effect.

The yield of toluene as a function of steam-coal ratio shows, like the yield of benzene, a definite minimum at a ratio of 1.25, although in this case neither the cracking temperature nor the retention time seem to be important.

The process variables have very little effect on the yield of styrene. It is relatively constant at about 6.0 pounds/ton.

The highest cracking temperatures and the longest retention times investigated favored the production of naphthalene. At a cracking temperature of 800°, the yield was 9.3 pounds/ton, while at 900° it increased to 13.9 pounds/ton. In the same way, increasing the retention time from 0.5 to 0.9 seconds increased the yield from 9.0 to 13.6 pounds/ton. The steam-coal ratio, on the other hand, seemed to have little effect.

Effect of Process Variables on Heavy Oil Produced

As expected, the higher cracking temperatures favored the conversion of the heavy oil to light oil and volatile gases. Surprisingly, however, there was a definite maximum in the yield at the intermediate retention time and the intermediate steam-coal ratio, that is, 0.7 seconds and a ratio of 1.25.

Some analytical work was done on the heavy oil, but due to its complex nature, no individual components were determined. The heavy oil is mainly aromatic in character and is composed of polynuclear aromatic hydrocarbons of high molecular weight. An ultimate analysis was made on the heavy oil from each run, but there was little difference. The average analysis is:

| | |
|---|---|
| Carbon | 90.35% |
| Hydrogen | 5.03 |
| Nitrogen | 1.46 |
| Sulfur | 0.67 |
| Ash | 1.36 |
| Oxygen (by diff.) | 1.13 |

Comparison of the Different Cannel Coals

In view of the fact that the yields of the commercially important products are, in general, not particularly sensitive to the process conditions in the ranges investigated, the four different cannel coals were compared at only a single set of conditions. A cracking temperature of 850°, an average retention time of 0.9 seconds, and a steam-coal ratio of 1.0 was chosen. While these conditions are not optimum, it seems unlikely that the comparison would be drastically different at any other generally-similar conditions. The results of these experiments are given in Tables 2, 3, 4, 5 and 6.

There is a good correlation between the yields of total gas, ethylene, total light oil, benzene, toluene, etc., and the gas and oil yield in the Fisher assay. When more gas and oil is obtained in the Fisher assay, a similar increase is noticed in the yields of the more valuable products. This is not, however, true with the yields of heavy oil. There is probably a tendency for the high assaying coals to produce more heavy oil, but the correlation is not nearly as high as it is for the light oils and gases.

## DISCUSSION

The low-temperature carbonization of cannel coal immediately followed by a thermal cracking of the volatile products produces excellent yields of ethylene, benzene, and other aromatic hydrocarbons. As expected, the yields of these products are much higher than could be obtained from lignite; over five times as much ethylene and benzene can be obtained. This did indeed result in a lower capital investment for a commercial plant producing the same amount of ethylene and aromatics as the lignite plant, and undoubtedly more than offset the increased cost of the cannel coal. A preliminary economic analysis, however, indicated that this process is still probably not competitive with the conventional crude oil cracking process. If the cost of crude oil should increase significantly, or if significant engineering improvements could be made to lower the capital cost, the commercial use of this process would be a possibility.

## REFERENCE

[1] R. S. Montgomery, D. L. Decker and J. C. Mackey, Ind. Eng. Chem., 51, p. 1293 (1959).

TABLE 2

Cracking Temperature: 850°C                Average retention time: 0.9 sec.
Steam-coal ratio: 1.0

Charge: 500 gms. of 3-1/2 - 10 mesh "Gay" cannel coal

| | | | |
|---|---|---|---|
| Yield of Gas: | 107.9 gms. | 431.0 lbs/ton | 502.6 lbs/ton(MAF) |
| Ethylene | 42.3 | 169.0 | 197.0 |
| Acetylene | 2.2 | 8.8 | 10.2 |
| Propylene | 4.3 | 17.2 | 20.0 |
| Butadiene | 1.7 | 6.8 | 7.9 |
| Butene-2 | 0.5 | 2.0 | 2.3 |
| Methane | 35.6 | 142.0 | 166.0 |
| Ethane | 3.1 | 12.4 | 14.4 |
| Hydrogen | 3.7 | 14.8 | 17.2 |
| Carbon monoxide | 11.2 | 44.8 | 52.2 |
| Carbon dioxide | 3.3 | 13.2 | 15.4 |
| Yield of Light Oil: | 23.7 | 94.8 | 110.3 |
| Benzene | | 18.2 | 21.2 |
| Toluene | | 10.4 | 12.1 |
| Styrene | | 5.7 | 6.6 |
| $C_2$ Benzenes | | 2.5 | 2.9 |
| Indene | | 4.9 | 5.7 |
| Indan/or methylstyrene | | 1.7 | 2.0 |
| Naphthalene | | 9.7 | 11.3 |
| Methyl naphthalenes | | 3.4 | 4.0 |
| Yield of Heavy Oil: | 53.0 | 212.0 | 247.0 |
| Yield of Char | 290.1 | 1160.0 | |

Heat Content of Gas: 747 BTU/cu.ft. (ethylene-free)

TABLE 3

Cracking Temperature: 850°C  Average retention time: 0.9 sec.
Steam-coal ratio: 1.0

Charge: 500 gms. of 3-1/2 - 10 mesh "Big Chief" cannel coal

| | | | |
|---|---|---|---|
| Yield of Gas: | 121.1 gms. | 484.0 lbs/ton | 509.4 lbs/ton(MAF) |
| Ethylene | 45.3 | 181.4 | 191.0 |
| Acetylene | 1.6 | 6.4 | 6.7 |
| Propylene | 6.6 | 26.4 | 27.8 |
| Butadiene | 2.7 | 10.8 | 11.4 |
| Butene-2 | 0.5 | 2.0 | 2.1 |
| Methane | 35.7 | 143.0 | 150.5 |
| Ethane | 2.9 | 11.6 | 12.2 |
| Hydrogen | 4.2 | 16.8 | 17.7 |
| Carbon monoxide | 16.7 | 66.0 | 69.4 |
| Carbon dioxide | 4.9 | 19.6 | 20.6 |
| Yield of Light Oil: | 26.6 | 106.2 | 111.5 |
| Benzene | | 29.9 | 31.4 |
| Toluene | | 11.9 | 12.5 |
| Styrene | | 4.5 | 4.7 |
| $C_2$ Benzenes | | 3.1 | 3.3 |
| Indene | | 6.0 | 6.3 |
| Indan/or methylstyrene | | 2.0 | 2.1 |
| Naphthalene | | 7.3 | 7.7 |
| Methyl naphthalene | | 3.0 | 3.2 |
| Yield of Heavy Oil: | 60.7 | 242.8 | 254.0 |
| Yield of Char: | 272.2 | 1088.0 | |

Heat Content of Gas: 728 BTU/cu.ft. (ethylene-free)

TABLE 4

Cracking Temperature: 850°C Average retention time: 0.9 sec.
Steam-coal ratio: 1.0

Charge 500 gms. of 3-1/2 - 10 mesh "Stollings" cannel coal

| | | | |
|---|---|---|---|
| Yield of Gas: | 123.0 gms. | 491.8 lbs/ton | 549.7 lbs/ton(MAF) |
| Ethylene | 46.5 | 186.0 | 208.8 |
| Acetylene | 2.7 | 10.8 | 12.1 |
| Propylene | 8.6 | 34.4 | 38.6 |
| Butadiene | 2.9 | 11.6 | 13.0 |
| Butene-2 | 0.5 | 2.0 | 2.2 |
| Methane | 33.9 | 135.6 | 152.3 |
| Ethane | 3.9 | 15.6 | 17.5 |
| Hydrogen | 3.7 | 14.8 | 16.6 |
| Carbon monoxide | 14.1 | 56.2 | 63.0 |
| Carbon dioxide | 5.7 | 22.8 | 25.6 |
| Yield of Light Oil: | 28.0 | 112.0 | 126.0 |
| Benzene | | 35.8 | 40.2 |
| Toluene | | 14.1 | 15.8 |
| Styrene | | 5.4 | 6.1 |
| $C_2$ Benzenes | | 4.3 | 4.8 |
| Indan/or methylstyrene | | 2.6 | 2.9 |
| Naphthalene | | 8.1 | 9.1 |
| Methyl naphthalene | | 3.6 | 4.0 |
| Yield of Heavy Oil: | 71.4 | 284.0 | 309.0 |
| Yield of Char: | 265.8 | 1063.0 | |

Heat Content of Gas: 784 BTU/cu.ft. (ethylene-free)

Montgomery

TABLE 5

Cracking Temperature: 850°C    Average retention time: 0.9 sec.
Steam-coal ratio: 1.0

Charge: 500 gms. of 3-1/2 - 10 mesh "Dorothy" cannel coal

| | | | |
|---|---|---|---|
| Yield of Gas: | 138.0 gms. | 552.2 lbs/ton | 587.9 lbs/ton(MAF) |
| Ethylene | 57.5 | 230.0 | 245.0 |
| Acetylene | 4.1 | 16.4 | 17.5 |
| Propylene | 9.6 | 38.4 | 40.8 |
| Butadiene | 3.4 | 13.6 | 14.5 |
| Butene-2 | 0.5 | 2.0 | 2.1 |
| Methane | 37.6 | 150.6 | 160.2 |
| Ethane | 5.0 | 20.0 | 21.3 |
| Hydrogen | 4.6 | 18.4 | 19.6 |
| Carbon monoxide | 9.2 | 36.8 | 39.2 |
| Carbon dioxide | 6.5 | 26.0 | 27.7 |
| Yield of Light Oil: | 33.5 | 133.8 | 142.3 |
| Benzene | | 43.8 | 46.6 |
| Toluene | | 16.7 | 17.8 |
| Styrene | | 6.3 | 6.7 |
| $C_2$ Benzenes | | 3.9 | 4.2 |
| Indene | | 7.7 | 8.2 |
| Indan/or methylstyrene | | 11.1 | 11.8 |
| Methyl naphthalenes | | 4.5 | 4.8 |
| Yield of Heavy Oil: | 65.1 | 260.2 | 277.0 |
| Yield of Char: | 236.1 | 944.0 | |

Heat Content of Gas: 794 BTU/cu.ft. (ethylene-free)

TABLE 6

Ultimate Analysis of Heavy Oil:

| | "Gay" | "Stollings" | "Big Chief" | "Dorothy" |
|---|---|---|---|---|
| Carbon | 90.26% | 89.58% | 87.42% | 88.40% |
| Hydrogen | 5.00 | 4.94 | 5.51 | 4.98 |
| Nitrogen | 1.35 | 1.57 | 1.38 | 1.74 |
| Sulfur | .62 | .74 | .74 | .84 |
| Ash | 2.01 | 1.60 | 1.30 | .66 |
| Oxygen (by diff.) | .76 | 1.57 | 3.65 | 3.38 |

Proximate Analysis of Char:

| | | | | |
|---|---|---|---|---|
| Moisture | 0.67% | 0.75% | 0.63% | 0.76% |
| Net volatile | 8.69 | 9.90 | 9.43 | 11.06 |
| Fixed carbon | 66.95 | 70.56 | 80.84 | 76.89 |
| Ash | 23.70 | 18.79 | 9.10 | 11.29 |

Ultimate Analysis of Char:

| | | | | |
|---|---|---|---|---|
| Hydrogen | 2.82 | 2.91 | 3.09 | 3.05 |
| Carbon | 68.70 | 71.73 | 81.63 | 79.59 |
| Nitrogen | 0.69 | 1.46 | 1.46 | 1.53 |
| Sulfur | 0.37 | 1.12 | 0.62 | 0.83 |
| Oxygen (by diff.) | 3.72 | 4.29 | 4.00 | 3.71 |

| | | | | |
|---|---|---|---|---|
| BTU/lb. of Char (MAF) | 14,350 | 14,680 | 14,865 | 14,900 |